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The Reaction of Acyl Halides with Aromatic Tertiary Amines

THE REACTION OF ACYL HALIDES WITH AROMATIC TERTIARY AMINES

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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THE REACTION OF AROMATIC TERTIARY AMINES WITH ACYL HALIDES

INTRODUCTION

The reaction of aromatic amines with acyl halides is used as a means of distinguishing between the various kinds of amines. Benzene sulfonyl chloride is the acid halide most generally used in carrying out the test. Tertiary aromatic amines as a rule do not react with benzene sulfonyl chloride, and by this property are distinguished from the primary and secondary amines. However, it has been found that dimethyl aniline interferes with this test, because it gives a reaction with benzene sulfonyl chloride. This reaction was studied in some detail by Wroby[1], who made it the subject for his bachelor's thesis.

In the present work, the reaction of different acyl halides with various amines was studied. Also the effect of different solvents on the rate of reaction was studied. The effect of increasing molecular weight on the ease with which groups could be replaced was also studied.

HISTORICAL PART

Hess[2] was the first man to study the reaction between benzoyl chloride and dimethyl and diethyl aniline. He refluxed dimethyl aniline and benzoyl chloride for several hours at a temperature of 190 C. A green dye was formed during the reaction. A yellow oil distilled over between 315-330° C from which a solid crystallized out on cooling. Yellow crystals, melting at 63° were obtained when the solid was recrystallized from ligroin. According to analysis the product was benzoyl methyl aniline. Diethyl aniline and benzoyl chloride were refluxed in a similar manner at 200° C for several hours. A green dye was also formed in the course of this experiment. The oil distilled at 260° C under 620 mm. pressure, and crystals separated after standing a long time over concentrated sulfuric acid. According to analysis, the solid obtained was benzoyl ethyl aniline, which has a melting point of 60° C.

Dehn[3] studied the reaction of benzoyl chloride with various amines in order to isolate the addition products. He used various amines and noted the fact that some of the amines reacted faster than others. Sunlight also promoted the reaction. Particular precautions were taken to keep reagents free from moisture as this causes the addition products to decompose.

Dehn[4] also studied the reaction between benzene sulfonyl chloride and amines in anhydrous ether. He found that tertiary amines with benzoyl chloride gave only one type of addition product. On the other hand, benzene sulfonyl chloride gave two kinds of addition products, which will be discussed later. He

isolated the various addition products and determined the amount of chlorine in the compounds.

Menschutkin[5] measured the velocities of reaction between triethyl amine and various aliphatic iodides in different solvents. He found the velocity of reaction varied with the different solvents, indicating that there is a distinct specific attraction between the solvent and the dissolved substance.

Hemptinne and Bekaert[6] also studied the effect of the solvent on the velocity of reaction. They used ethyl bromide with triethyl amine, using benzene, xylene, chlorbenzene, acetone, methyl-, propyl-, benzyl alcohols, with various mixtures of liquids. It was found that in a mixture of compounds of similar nature, such as two alcohols, the velocity of reaction could be calculated approximately from that determined for each liquid separately. However, in mixtures containing alcohol and some other liquid, the velocity far exceeded that calculated from the mixture rule. The results check fairly well with results obtained by Menschutkin for benzene, acetone, chlorobenzene, and xylene, but are considerably less for the alcohol.

Long[7] measured the velocities of the reaction of alkyl bromides with pyridine and allied cyclic tertiary bases. He found that isoamyl bromide reacts with pyridine, - and - picoline, and quinoline about seven times, and isopropyl about three times as rapidly as with isobutyl bromide.

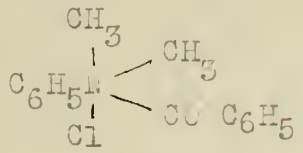
Preston and Jones[8] determined the velocity constants for reaction in absolute alcohol between methyl iodide, ethyl iodide, propyl iodide, allyl iodide, o, m, p-methyl benzyl bromide, o, m, p-bromo benzyl bromide; ~~with~~ and dimethyl aniline and tri-, iso-amyl

amine. They found that the reactivities of the halides depend on the structure of alkyl groups and are only slightly influenced by the base with which they react.

Olivier[9] studied the effect of variously substituted sulfonyl chlorides on velocity constants in their reactions with benzene and aluminium chloride. He found the influence is considerable whether the substitution is in the hydrocarbon ring or in the ring of the acid chloride and is more pronounced in the latter case. The constants for $ClC_6H_4SO_2Cl$ and $BrC_6H_4SO_2Cl$ are nearly identical. By using benzene as the solvent and one mole of the acid chloride and one mole of $AlCl_3$, the reaction is mono molecular and the constant is proportional to the amount of $AlCl_3$ added.

THEORETICAL PART

C_6H_5COCl adds to $C_6H_5N(CH_3)_2$ in the following manner



This is probably the first step in the reaction. Dehn[3] claims to have isolated this compound as well as the diethyl aniline benzoyl chloride. He determined the amount of chloride present in the compound. Sunlight hastens the action. He thinks the base combines in the following manner:

1. $R_3N + ClOCC_6H_5 = R_3N \cdot ClOCC_6H_5$

2. $R_3N + ClOCC_6H_5 = R_3(COC_6H_5)NCl$

The rearrangement from 1 to 2 is probably caused by the action of the sunlight. The weak part of this hypothesis was the fact that he couldn't isolate two isomeric addition products. Since secondary reactions do not occur with the tertiary bases, it was thought they were best suited for study. Tertiary bases, however, he observed, precipitate two crystalline forms which were assumed to be the benzoyl chloride and hydrogen chloride addition products. Since hydrogen chloride could not be formed except by hydrolysis of benzoyl chloride, the absolute exclusion of water will eliminate the formation of the hydrochloride. The following equations show how the various addition compounds decompose.

3. $(CH_3C_6H_4BzNHHCl) \xrightarrow{\text{heat}} CH_3C_6H_4BzNH + HCl$

4. $RBzNHHCl + H_2O = RBzNH + H_2O + HCl$

5. $R_2BzNHCl + H_2O = R_2BzN + H_2O + HCl$

6. $R_3BzNCl + H_2O = R_3N + BzOH + HCl$

The following are the various types of addition products which are formed by the interaction of tertiary amines with benzene sulfonyl chloride.

(a) $C_6H_5SO_2Cl \quad R_3N$

(b) $C_6H_5SO_2Cl \quad (R_3N)_2$

(c) $C_6H_5SO_2Cl \quad (R_3N)_3$

(d) $(C_6H_5SO_2Cl) \quad R_3N$

Dehn[4] found that benzene sulfonyl chloride gave addition compounds of the type (a) and (b), differing from acetyl chloride and benzoyl chloride which gave addition compounds of the type (a) only.

Traces of moisture cause the following reactions to take place:

7. $C_6H_5SO_2Cl \; R_3N + H_2O = C_6H_5SO_3H \quad R_3N \; HCl$

8. $C_6H_5SO_2CH + R_3N = C_6H_5SO_2CH.R_3N$

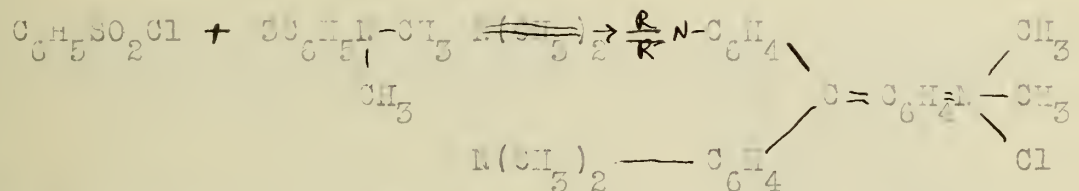
The reactions are non ionic as proved by the following results. Benzene sulfonyl chloride yields the addition compound with aniline and toluidines, but hydrogen chloride fails to give their corresponding tertiary compound the same or any addition product.

9. $C_6H_5SO_2Cl + C_6H_5NH_2 = C_6H_5SO_2 \; N \; \begin{matrix} C_6H_5 \\ H \quad H \end{matrix} \; Cl$

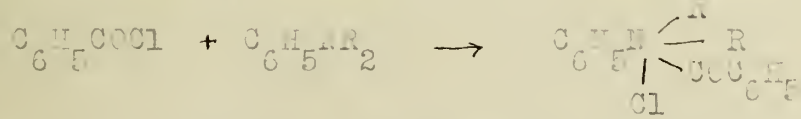
10. $C_6H_5SO_2NH$ / C_6H_5 HCl No reaction

In the first case (9), a break is necessary between the $C_6H_5SO_2$ and Cl, while in the second case (10), a break between H and Cl. Now the break between RSO_2 and Cl is much easier than the break between H and Cl, since by heat alone $C_6H_5SO_2Cl$ can be decomposed. Since HCl fails to yield the addition compound the conclusion is that HCl does not ionize in absolute ether, and the additive reactions are therefore non-ionic.

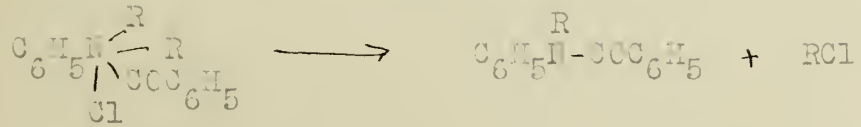
Quinoline, quinaldine, acridine, and tribenzyl amine add two molecules of the base to one molecule of benzene sulfonyl chloride. This was determined by an analysis for the amount of chloride present. A blue dye was produced by refluxing benzene sulfonyl chloride and dimethyl aniline. This dye, no doubt, is methyl violet. Haasencamp[10] accounts for it's formation in the following manner:



The following is the way, probably, the reaction between benzoyl chloride and tertiary amines takes place.



Then upon heating, the addition product breaks down in the following manner, with RCl splitting off.



In measuring the velocity constants it may be that the rate of decomposition of the addition product is found instead of the rate of combination of the amine with the acid chloride. Any unchanged acid chloride will give two moles of acid on decomposition.

$$C_6H_5COCl + H_2O = C_6H_5CO_2H + HCl$$

$$C_6H_5SO_2Cl + H_2O = C_6H_5SO_3H + HCl$$

Benzoic acid is formed during the distillation of benzoyl butyl aniline by the decomposition of the addition product in the presence of moisture

$$C_6H_5N\begin{matrix}R\\R\\COC_6H_5\\Cl\end{matrix} \xrightarrow[H_2O]{\text{heat}} C_6H_5NR_2 + C_6H_5CO_2H + HCl$$

The green dye formed in the refluxing of benzoyl chloride and dibutyl aniline is probably the result of the following reaction:

$$2C_6H_5N(C_4H_9)_2 + C_6H_5COCl = C_6H_5C(=C_6H_4{=}N{-}C_4H_9)(Cl)(C_4H_9)\text{—}C_6H_4N(C_4H_9)_2$$

EXPERIMENTAL PART

Fifty grams of dibutyl aniline and thirty grams of benzoyl chloride were placed in a 200 cc. round bottom flask and the mixture refluxed for several hours. Some yellow crystals were formed in the bottom of the flask before the mixture had been heated. Upon raising the temperature, the solution became dark green, ~~which~~ as Hess had noted in his work with dimethyl and diethyl aniline. The mixture boiled around 180° C (as was determined by a thermometer suspended by a copper wire in the flask). The solution was allowed to cool and treated with stong NaOH solution. The purpose of the NaOH solution was to destroy any unchanged benzoyl chloride. The NaOH solution was separated by means of a separatory funnel and the green liquid distilled under diminished pressure. On this, the pressure was not taken. A white solid came over between 170-180° C. This was taken up in ether solution, and treated with NaOH solution. The NaOH was neutralized with dilute HCl, and the solid was washed and recrystallized from hot water. The melting point of the crystals was 119-120°, which agrees with the melting point of benzoic acid. 22 grams of the liquid came over between 185-210° C. This was dibutyl aniline which resulted from decomposition of the addition product or from some unchanged dibutyl aniline in the experiment. The next fraction was from 210-260° C, and weighed 16 grams. The liquid was very viscous, insoluble in acid, and alkali, and soluble with difficulty in alcohol, and ether. The evidence proved it to be benzoyl butyl aniline, since it had properties similar to methyl and ethyl benzoyl aniline. Hess found that $C_6H_{11}-NCOC_6H_5$ (with CH_3 below the C_6H_{11})

was only slightly soluble i alcohol.

In a second experiment, 50 cc. dibutyl aniline and 50 cc. of benzoyl chloride were placed in a 200 cc. round bottomed flask and mixture refluxed four hours. The mixture was allowed to stand over strong NaOH solution for a day to destroy excess benzoyl chloride. The green solution was then distilled under diminished pressure. The green solution soon turned dark brown showing that the green dye had decomposed under action of heat. The solution started boiling at 148° under 30 mm. pressure. The liquid was taken in two fractions, 148-217°; 220-235°. The first fraction was acidified with HCl to test whether the oil was dibutyl aniline. The liquid turned dark red and became very viscous. It would not solidify out on cooling with freezing mixtures. The second fraction, 220-235°, was a golden yellow liquid, which upon cooling separated out yellow crystals. It was thought at first, that the solid might be benzoic acid, and the liquid, dibutyl aniline from the decomposition of the addition product. However, when the solution was taken up in ether and treated with NaOH solution several times, it was found that the solid was not benzoic acid. This was proved by the fact that upon neutralizing the NaOH, no precipitate was formed. If the solid had been benzoic acid, there would have been precipitation upon acidifying the NaOH solution. The solid was recrystallized twice from ligroin, and the melting point of the pure crystals was 52-53° C.

20 grams were obtained which is about a 20% yield. The solid was analyzed and chlorine was found to be absent, and nitrogen present. Dibutyl aniline was also refluxed with acetic anhydride, but no reaction took place, for 20 cc. of acetic anhydride

were recovered, and only 23 cc. of acetic anhydride were put into the original solution.

Determination of Velocity Constants.

Standard HCl solution, 80% alcoholic NaOH solution were made and factors determined. Also the time for complete reaction of benzoyl chloride with the alkali was determined. It was found that standing over night was sufficient time for complete reaction.

The Reaction Velocity of Benzoyl Chloride and Dibutyl Aniline.

One fourth mole of dibutyl aniline, and one fourth mole of benzoyl chloride were dissolved in benzene and made up to 500 cc. Five cc. of the mixture were drawn off for analysis before starting the reflux.

Time in minutes.	cc. NaOH used N factor .217	cc. HCl used N factor .262
0	25	3
30	25	3.45
60	25	3.15
120	25	3.00
240	25	2.75
300	25	2.15
360	25	2.7

The results show that no reaction took place at a temperature of 82°C. Several indicators were used in titration, and phenolphthalein was found to give the best results. The benzene was distilled off, and the mixture allowed to reflux for several hours. Some benzoyl butyl aniline was obtained in the same manner as

before. The melting point of the recrystallized solid was 53-54° C.

The Reaction of Benzoyl Chloride with Dibutyl Aniline in Xylene Solution.

One eighth of a mole of dibutyl aniline, and one eighth of a mole of benzoyl chloride were dissolved in xylene, and the solution made up to 250 cc. Five cc. portions were drawn off from time to time, and analyzed.

Time in minutes	cc. NaOH used N factor .217	cc. HCl used N factor .262
0	15	0.5
30	15	0.45
60	15	0.45
120	15	0.65
180	15	0.55

Results show there was no reaction between benzoyl chloride, and dibutyl aniline in xylene solution.

The Reaction Between Dimethyl Aniline and Benzene Sulfonyl Chloride.

One eighth of a mole of each of the interacting substances were dissolved in benzene and made up to 250 cc.

Tables follow on the next page.

Run Number One.

Time in Minutes	cc. NaOH used N factor .261	cc. HCl used N factor.262	C_1 for mono-mol. react.	C_2 for di-mol. Reaction.
0	25	8.3		
60	25	8.8	5.02×10^{-4}	3.08×10^{-5}
120	25	8.85	2.78×10^{-4}	1.7×10^{-5}
180	25	9.10	2.78×10^{-4}	1.7×10^{-5}
270	22.65	8.40	5.87×10^{-4}	3.79×10^{-5}
360	20	6.05	5.00×10^{-4}	4.13×10^{-5}
450	20	6.75	5.13×10^{-4}	3.47×10^{-5}
540	15	2.70	5.64×10^{-4}	3.96×10^{-5}
630	15	3.00	5.22×10^{-4}	3.72×10^{-5}

Run Number Two.

0	25	11.1		
120	25	11.7	3.73×10^{-4}	2.71×10^{-5}
180	25	12.0	3.72×10^{-4}	2.77×10^{-5}
240	23	10.9	5.84×10^{-4}	4.47×10^{-5}
290	20.8	9	5.61×10^{-4}	4.43×10^{-5}
347	20	8.75	6.09×10^{-4}	4.88×10^{-5}
382	21	10.1	6.37×10^{-4}	5.20×10^{-5}

The Reaction Between Dibutyl Aniline and Benzene Sulfonyl Chloride.

One eighth of a mole of each was dissolved in benzene and the solution was made up to 250 cc.

Time in Minutes	cc. NaOH used N factor .261	cc. HCl used N factor.262
0	25	8.8
120	25	8.45
210	25	9.25
300	25	8.30
380	25	9.40
456	25	9.30

The results show that there was no reaction between dibutyl aniline and benzene sulfonyl chloride.

The Reaction Between Diethyl Aniline and Benzene Sulfonyl Chloride.

Time in Minutes	cc. NaOH used N factor .261	cc. HCl used N factor.262	C_1 for mono-mol. react.	C_2 for di-mol. Reaction.
0	25	10.9		
120	25	11.2	1.76×10^{-4}	1.29×10^{-5}
180	25	11.9	4.09×10^{-4}	3.02×10^{-5}
240	20.15	7.65	4.15×10^{-4}	3.11×10^{-5}
290	20	7.75	4.78×10^{-4}	3.68×10^{-5}
345	20	7.90	4.40×10^{-4}	3.39×10^{-5}
375	20	8.0	4.28×10^{-4}	3.30×10^{-5}

SUMMARY

1. Benzoyl butyl aniline was isolated from reaction of benzoyl chloride and dibutyl aniline.

2. Benzoyl chloride did not react with dibutyl aniline in benzene or xylene solutions at the boiling point of the solution.

3. Benzene sulfonyl chloride did not react with dibutyl aniline in benzene solution at a temperature of 55° C.

4. Benzene sulfonyl chloride reacts with dimethyl aniline and diethyl aniline in benzene solution at a temperature of 82° C. The methyl group is displaced a little easier than the ethyl group.

5. The velocity constants check for a mono-molecular reaction, indicating that the rate of decomposition of the addition compound formed by the interaction of the amine and the acid chloride was measured.

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